A STUDY OF THE DECOMPOSITION OF SILICATES BY BARIUM SALTS

BY
GILBERT HAYES WHITEFORD

DISSERTATION

Submitted to the Board of the University Studies of
The Johns Hopkins University in Partial
Requirement for the Degree of
Doctor of Philosophy
June, 1917

STANFORD UNIVERSITY LIBRARIES
WITHDRAWN

781
.65W
UNCLASSED

A STUDY OF THE DECOMPOSITION OF SILICATES BY BARIUM SALTS

BY
GILBERT HAYES WHITEFORD

DISSERTATION

Submitted to the Board of the University Studies of
The Johns Hopkins University in Partial
Requirement for the Degree of
Doctor of Philosophy
June, 1917

COURIER PRESS
Fort Collins,
Colo.

TABLE OF CONTENTS

	Page
Acknowledgment	4
Introduction	5
Purification of Reagents	6
Eutectic Mixture of Barium Carbonate and Chloride	7
Decomposition	8
Determination of Silica	9
Residues from Silica	10
Determination of Iron and Alumina	11
Determination of Calcium	12
Method for Separation of Calcium from Barium	15
Determination of Alkalis	16
Determination of Magnesium	20
Summation of Analyses	21
Conclusions	24
Biography	26

ACKNOWLEDGMENT

The investigation described in the following pages was suggested by Prof. J. C. W. Frazer and carried out under his direction. Whatever of merit there may be in the work is to be ascribed to his constant attention and suggestion. To him the author is deeply indebted. The author also wishes to thank Prof. Edward B. Mathews and Dr. J. T. Singewald for material for analysis and helpful suggestions; also Professors Morse, Reid, Lovelace and Gilpin, and Dr. Davis for kindly interest and helpful instruction throughout his course.

A Study of the Decomposition of Silicates by Barium Salts

Among the numerous reagents for the decomposition of silicate rocks both barium carbonate and barium chloride have been used separately. According to J. Lawrence Smith*, "The chlorid of barium has been lately proposed; but its decomposing properties are very feeble, as the chlorine in combination with the barium is not liberated at a white heat, and few silicates are able to produce the decomposition. It may succeed with some of the feldspars, but decomposes very imperfectly even the micas. So it is rather a risk to employ it with an unknown substance.

The carbonate of baryta is the compound of baryta most generally employed for silica decompositions; still this is attended with much difficulty, owing to the infusibility of this salt, and the impossibility of driving off the carbonic acid by heat alone; and even if this latter were possible, the objection pertaining to caustic baryta would then arise.

The following extract from Rose's Analytical Chemistry, (translation by Normandy, in a note by the translator), presents fairly the difficulties attending the method of decomposing the silicates:

'The heat applied is so intense that some precautions must be taken. The platinum crucible containing the mixture should be exposed first to the heat of an argand-lamp, and when the mass begins to agglutinate, the crucible should be closed, and its cover tied down with platinum wire, then placed in a Hessian crucible, closed up also; the whole is placed upon an inverted crucible, and submitted to the action of a blast of a wind furnace, beginning first gradually with a red heat, piling on more coke, so as to fill up the furnace, and increasing the heat to the highest possible pitch, until the Hessian crucible begins to soften. It is absolutely necessary to the success of the operation, that the Hessian crucible should be closed as well as possible, which is best done by luting the cover with fire-clay; the Hessian crucible and its cover having fused together, cannot be separated, except by breaking, etc., etc.'

* J. Lawrence Smith, Am. Jour. Sci., 2nd Series, **15**, 235, (1853).

It will be seen in reading this axtract, that the heat required is not ordinarily at the command of most chemists, in fact, no other variety of furnace than a Sefstroem can be depended on for a complete decomposition."

In a recent investigation Hempel* decomposed the most refractory silicates by heating in a specially constructed oven and blast furnace at 1360°. Hempel, however, records no analyses of the silicates he decomposed in this way.

The purpose of this investigation was to effect a complete decomposition at a lower temperature by using a mixture of barium carbonate and chloride and to compare the analytical advantages of the method with the methods in general use at present.

PURIFICATION OF REAGENTS

Barium Chloride.—The purest commercial barium chloride was dissolved in distilled water, filtered and reprecipitated by a current of hydrochloric acid gas which was made to pass through two wash bottles. It was again dissolved and reprecipitated in the same way. After washing with a very small quantity of water, it was filtered on a Witte filter and dried to constant weight. To obtain the anhydrous chloride it was heated in the muffle furnace to constant weight.

Barium Carbonate.—The hydrous chloride prepared as above was dissolved in water, the solution made ammonical and the carbonate precipitated by a current of washed carbon dioxide gas. The precipitate was then washed by decantation until practically free from chlorides, collected on a Witte filter and washed until the washings gave no precipitate with silver nitrate. It was then dried in the electric oven at 150° until a constant weight was obtained.

Sodium Carbonate.—"Chemically pure" crystals were dissolved in distilled water, the solution boiled and filtered. It was then put in a thick-walled flask and precipitated under pressure by a current of washed carbon dioxide gas. The precipitated bicarbonate was then dried as much as possible on a suction filter and finally heated in an air bath to constant weight.

Calcium Carbonate.—The purest commercial chloride was dissolved in distilled water, a little ammonium dydroxide added, the solution boiled and filtered on cooling. It was then precipitated by ammonium corbonate which had been made by passing washed carbon dioxide gas into ammonia. The precipitated calcium car-

* Hempel Zeit. f. Anal. Chem. **52**, 86, (1913).

bonate was then washed a number of times by decantation, collected on a porcelain filter, washed until free from chlorides and dried to constant weight.

Ammonium chloride.—This was made by dissolving washed hydrochloric acid gas in distilled water and neutralizing with ammonia gas made by boiling concentrated ammonium hydroxide. After filtering it was dried to constant weight.

Hydrofluoric acid.—This was tested by evaporation in a platinum crucible. No non-volatile residue was found.

Sulphuric acid.—The method of Fresenius was used. Three grams of ammonium sulphate were added to a liter of sulphuric acid and the solution heated in an evaporating dish until copious fumes were evolved. After cooling 5 grams of manganese dioxide were added and the acid again heated to boiling. On cooling it was placed in a retort and distilled. The first portion of the distillate was discarded and the remainder redistilled until no non-volatile residue remained after the evaporation of 3 to 5 cc. portions.

EUTECTIC MIXTURE OF BARIUM CARBONATE AND CHLORIDE

The melting point of anhydrous barium chloride is given by different investigators† as follows:

922° Myer, Riddle and Lamb, (1893).
847 Le Chatelier, (1887).
915.6 Mc Crae, (1895), by Pt-PtIr.
844 Ramsay and Eumorfopoulos, (1896).
960 Ruff and Plato, (1903).

The melting point of barium carbonate, according to Le Chatelier*, (1887), is 795°.

In order to secure decomposition at the lowest temperature possible, the composition of the eutectic mixture was determined. The melting points obtained, however, are only approximate, since the two salts when mixed appeared to have no definite melting point. A platinum-iridium junction protected by a thin platinum sleeve was placed in the center of the mixture and the crucible heated in the Morse electric furnace. An attempt to plot the melting and cooling curves was made, but this had to be abandoned since no definite breaks in the curve either on melting or on cooling were noted. The covers were then removed from the furnace and the temperatures at which the mix-

* Le Chatelier, Bull. Soc. Chem. **47**, 301, (1887).
† Landolt-Bornstein, Physik.-chem. Tarbellen, 270.

ture began to melt and to solidify were noted. In this way the eutectic point was determined with a reasonable degree of accuracy, though, as stated, the temperatures given below are only approximate.

$BaCO_3$ moles	$BaCl_2$ moles	Melting Point
1.0	.67	740°
1.0	1.0	700
1.0	1.1	720
1.0	1.5	725

DECOMPOSITION

The eutectic mixture was not used for the decomposition because some of the carbonate ions are used up during the decomposition, thus changing the composition of the mixture. It is therefore advantageous to start with a considerable excess of the carbonate and allow the eutectic point to be approached during the decomposition. The following tests were made with one-gram samples of Websterite in order to determine the best ratio to mix the carbonate and chloride, the amount of the mixture necessary to effect a complete decomposition and the length of time necessary to heat in the flame of the ordinary Bunsen burner.

Amt. of mixture	Ratio in moles $BaCo_3$	$BaCl_2$	Time heated	State of decomposition
4 grams	1	1	15 min.	Gritty residue
4 "	1	1	15 "	" "
4 "	2	1	30 "	" "
4 "	2	1	30 "	" "
4 "	3	1	30 "	" "
4 "	4	1	30 "	" "
5 "	4	1	30 "	No " "
5 "	4	1	50 "	" " "

The rock powder was ground in an agate mortar until all particles passed through a sieve of the finest silk bolting cloth. In all tests the finely ground rock powder was intimately mixed with the decomposition mixture by thorough grinding in the mortar. A small amount of the mixture of barium salts being used as a pad in the bottom of the crucible, then the rock powder with the mixture and finally on top of this a little of the mixture which was reserved to rinse off the watch glass and the mortar. The heat of an ordinary Bunsen burner, producing a dull redness as far up the crucible as the mixture extends is sufficient to sinter the mass together and produce complete decomposition. A higher heat, as will be shown later, is advantageous, since it decreases the adsorption power of the silica. The mass need not fuse, but by simply sintering together, produces a cake which is very easily removed

by the gentlest tapping on the bottom of the crucible. This has a distinct advantage over the usual method of fusing with sodium carbonate, since all loss by spattering out of the crucible during the fusion is avoided. If too high a heat is used in the decomposition, a fusion takes place which in some cases requires considerable time to remove from the crucible.

Anhydrous barium chloride must be used, otherwise, the barium chloride will hydrolize at the high temperature and the crucible may be badly attacked by the hydrochloric acid in contact with air. In one case after the crucible was cleaned a loss of over two-tenths of a gram in weight was noted; while, due to the dissolved platinum, the fused mass was badly discolored and unfit for analysis. With the anhydrous salt the platinum crucibles were never attacked, and even with two or three hours heating to a bright redness no loss in weight and no discoloration could be detected. In two cases the fusion sodium carbonate slightly attacked the crucible, while in the decomposition with the barium salts the crucible was not attacked.

ANALYSIS

Silica

One-gram samples of the rock powder were used in each case. This was intimately mixed with five grams of the barium salts in the ratio of four moles of barium carbonate to one mole of anhydrous barium chloride and decomposed in the heat of an ordinary Bunsen burner. The sintered mass was dissolved in dilute hydrochloric acid and evaporated to dryness twice on the water bath. Transparent quartz dishes were used for this evaporation, 10% hydrochloric acid was used to moisten the silica. This is believed to be advantageous since it in no case renders the silica gelatinous as is frequently the case when too great an excess of the concentrated acid is used. After filtering, washing, igniting to constant weight and evaporating with hydrofluoric acid in the usual way, Lenher's* method of treating the residue was used. That is, instead of putting the precipitate of iron, alumina, etc., into the unwashed crucible, the residue from the evaporation of the hydrofluoric acid and assuming that all of this residue consisted of oxides of the aluminum group, the residue was fused with a small amount of sodium carbonate, the fusion taken up with a little dilute hydrochloric acid and added to the filtrate from the silica. This is more accurate since all matter adsorbed on the silica is not aluminum and ferric oxides, and in case a large amount of iron be present it

*Lenher and Truog. J. Am. Chem. Soc. 38, 1050 (1916).

may not all be in the ferric state. A comparison of the results obtained by this method and by the ordinary method of decomposing with sodium carbonate is given in the following table:

	Sample	% SiO_2 Na_2CO_3	Ba salts
1	Tourmaline	39.06	39.16
2	Websterite	52.18	52.18
3	Meta-rhyolite	76.61	76.51
4	Gneissic inclusion	78.05	77.99
5	Light band in gneiss	69.70	69.67
6	Queleuzite	9.39	9.38
7	Garnet rock	37.01	37.07

Residues.—Silica always adsorbs iron, aluminum and other salts and no amount of washing will completely remove these from its surface. It was noticed that while decomposition was complete at a dull redness, the amount of adsorbed matter could be greatly reduced in some cases by heating to a higher temperature. To study the relation between the temperature and the amount of adsorbed matter another series was run at the full heat of the Morse electric furnace,—about 900°. The following table shows the results:

RESIDUES.

Sample	Na_2CO_3 decomp.	Ba salts decomp. Dull red	Elect. furnace
1	.0070	.0119	.0101
2	.0045	.0342	.0072
3	.0068	.0111	.0083
4	.0111	.0203	.0135
5	.0065	.0243	.0128
6	.0186	.1603	.0153
7	.0023	0215	.0185

No real advantage seems to be gained by the use of high temperatures in the decomposition other than to decrease this residue, except in the case of No. 6,—a garnet rock very rich in manganese. In the case of this specimen accurate checks of SiO_2 could not be obtained with so large a residue, while, when decomposed at a high temperature, it was quite easy to check the results within the limits of experimental error. With sodium carbonate this fusion strongly attacked the crucible, forming a dark coating which only could be removed by long and repeated heatings with concentrated hydrochloric acid. The fusion with barium salts did not attack the crucible at all, not even discoloring it. In all cases the mass decomposed at higher temperatures formed a loosely sintered mass which was easily revomed from the crucible, could easily be broken up with a stirring rod and readily went into solution—in some cases without any evolution of carbon dioxide when treated with hydrochloric acid.

In order to determine if the amount of barium salts used in the decomposition had any relation to the amount of the residue, one decomposition was made using eight grams of barium salts instead of five, and heating to the full heat of the electric furnace. A difference of only .0001 gram was found in the amount of the residue.

ALUMINIUM AND IRON OXIDES

In precipitating iron and aluminum as hydroxides the use of methyl red to show the end point as suggested by Blum* was tried. When, however, the amount of ferric oxide is large, unless the amount of the solution is correspondingly large, considerable time is lost in waiting for the precipitate to settle in order to be able to see the color of the solution. In samples No. 6 and No. 7, silicates rich in manganese, the color of the indicator was destroyed as soon as it touched the solution, thus rendering methyl red useless in these cases. In these samples even a cubic centimeter of the methyl red did not impart the slightest color to the solution; in all other cases one or two drops gave the solution a distinct color.

In order to determine the end point a small piece of red litmus paper was moistened and placed on the convex side of the watch glass. When the precipitation was apparently completed by slowly dropping ammonium hydroxide from a burette into the hot solution, the supernatant vapor was blown off two or three times and the watch glass placed over the beaker. In this way the iron and aluminum hydroxides were completely precipitated.

Tests made on the fiiltrate showed that none of the aluminum hydroxide was redissolved. As soon as sufficient ammonium hydroxide was added to turn the color of the litmus paper, the contents of the beaker were boiled for one minute, the precipitate allowed to settle, then filtered and washed—first with ammonium chloride solution, (1%), then with water. The filter paper with the precipitate was then put back in the original beaker, dissolved in nitric acid and reprecipitated in the same way.

Instead of igniting the precipitate of ferric and aluminum hydroxide in the unwashed crucible containing the residue left from the evaporation of the silica by hydrofluoric acid, (the usual method), Lenher's† method was used, as described under silica. If the residue consisted entirely of the oxides of this group this would be unnecessary, but in the cases of some silicates the amount

*Blum. J. Am. Chem. Soc. **38**, 1282 (1916), Scientific Paper No. 286, U. S. Bureau of Standards.

†Lenher and Truog. J. Am. Chem. Soc. **38**, 1050 (1916).

of other substances in this residue is considerable. This was found to be especially true in the cases of samples No. 6 and No. 7, manganese silicates. In the case of these a large part of the residue from the silica consisted of manganese salts. Lenher's modification of the usual method is undoubtedly more accurate than the old way.

In the case of manganese silicates no trouble at all was experienced in separating the iron, alumina, etc., from the manganese. Qualitative tests were made, and it was found that when the end of the precipitation of the iron and alumina by the above method was observed an excess of a number of drops of the ammonium hydroxide could be added without bringing down any manganese hydroxide. Some of the reprecipitated iron and alumina was dissolved, was tested and found to be free from manganese. Some manganese could be found in the first precipitation, but this is, no doubt, due to the fact that the precipitate cannot be entirely freed from soluble salts by washing alone. Some manganese remains in the precipitate just as some calcium and magnesium remain, and the manganese is completely removed in the reprecipitation, just as the other soluble salts are. This fractional precipitation has the advantage of saving considerable time in the analysis.

Titanium oxide was determined by Weller's* colorometric method. The other elements which come down by this group were determined by the usual methods.

The difference in the results obtained from the two decompositions was very slight, as is shown in the following table:

	Total Fe as Fe_2O_3		Al_2O_3		TiO_2	
Sample	Na_2CO_3	Ba Salts	Na_2CO_3	Ba	Na_2CO_3	Ba
1	.0117	.0111	31.59	31.64	.0078	.0078
2	.1409	.1402	.0491	.0501	.0064	.0064
3	.0297	.0297	.1273	.1283	.0020	.0020
4	.0342	.0342	.1027	.1039	.0066	.0066
5	.0574	.0374	.1148	.1164	.0112	.0112
6	.0380	.0380	.0286	.0264	.0029	.0029
7	.0799	.0799	.1944	.1932	.0109	.0109

In the above table the ferric oxide represents the total iron in the sample calculated as ferric oxide. The greater part of this iron in all the samples existed in the ferrous state, but as this had to be determined by decomposition with hydrofluoric acid, this need only be shown in the summations of the separate samples.

CALCIUM

Numerous methods have been proposed for the separation of barium and calcium. However no one seems to have worked with

*Weller, Ber. 2593. (1882).

so small an amount of calcium in the presence of so large an amount of barium. In order to get a method which is at the same time accurate and rapid, a number of experiments were tried.

Rose* states that both the barium and calcium may be precipitated from the solution as sulphates, the mixed sulphates then treated with sodium, potassium or ammonium carbonate and the calcium sulphate will be converted quantitatively into calcium carbonate, while the barium sulphate will be unacted upon. Although Rose states that the reaction will be complete at the end of about six hours, it was found to give low results, even though allowed to stand 30 days with stirring at frequent intervals. Equilibrium between the sulphate and carbonate is reached so very slowly, as is shown by the following table, that this method is worthless.

$BaCO_3$	CaO taken	CaO found	Mixture stood
4.0 grams	0.1	.0807	over night
4. "	0.1	.0877	5 days
4. "	0.1	.0924	30 days

The method of simultaneous precipitation was next tried. An amount of sulphuric acid about 10% in excess of that which is necessary to precipitate all of the barium was neutralized with sodium carbonate and then about 50% excess of sodium carbonate added to the dilute solution of the sodium sulphate and the solution boiled. The precipitant while still hot was added, drop by drop, to the boiling solution of the barium and calcium chlorides, which was stirred vigorously all the while. After cooling and allowing to stand long enough for the barium sulphate to become granular, the mixture of barium sulphate and calcium carbonate was filtered and washed. The filter paper containing the precipitate was then spread out against the back of the beaker and the precipitate completely washed back into the beaker by a jet of water from the wash bottle. This was then treated from one to two hours with dilute hydrochloric acid, refiltered and thoroughly washed. The calcium, now all in the filtrate, was precipitated as oxalate. In all cases except one low results were obtained.

$BaCO_3$ used	$CaCO_3$ used equal to CaO	CaO found
4.0 grams	0.1785	0.1	.0981
4.0 "	.1785	.1	.0976
4.0 "	.1785	.1	.0981
5. "	.0179	.01	.0116
5. "	.0357	.02	.0195
5. "	.0535	.03	.0286
5. "	.0892	.05	.0492
5. "	.1785	.10	.0948
5. "	.2677	.15	.1480
.00 "	.1785	.10	.1001
.00 "	.1785	.10	.1001

* Rose, Analyse Quantitative, 37-40.

The method of Sidersky*, substituting ammonium oxalate for sodium carbonate was then tried, the process being carried out in the same manner. Results were as follows:

$BaCO_3$ used	$CaCO_3$ used equal to CaO	CaO found
5 grams	0.0178	0.0096
5 "	.0387	.0191
5 "	.0525	.0288
5 "	.0892	.0479
5 "	.1785	.1001
5 "	.2677	.1512

It is noticeable that the first part of the series is regular, though low. The last one of the series ran high. This may be due to the fact that the amount of hydrochloric acid used to dissolve the calcium oxalate was roughly estimated, and too large an excess being used, some of the barium sulphate was dissolved, as it is a well known fact that some barium sulphate will dissolve in strong hydrochloric acid. It is more likely, however, that the high results are due to the fact that some of the barium sulphate ran through the filter, since in almost all the barium sulphate, after treatment with hydrochloric acid, was exceedingly hard to filter.

A series was now tried by precipitating the barium and calcium as oxalates and then converting the barium oxalate to barium sulphate by a solution of ammonium sulphate containing an amount of sulphate ions just in excess of the theoretical amount necessary. Since the results obtained were varying, a number of experiments were made to determine the length of time necessary to convert the barium oxalate quantitatively to sulphate and also the time necessary to treat the calcium oxalate in the mixture with hydrochloric acid to convert it to calcium chloride.

$BaCO_3$ used	$CaCO_3$ used	Equals CaO	Time to convert BaC_2O_4 to $BaSO_4$	Time HCl	CaO found
5 grams	0.1785	0.1	over night	2 hours	.0997
"	"	"	" "	48 "	.1010
"	"	"	1 hour	2 "	.0999
"	"	"	20 hours	2 "	.0999
"	"	"	2 "	1½ "	.0995
"	"	"	3 "	over night	.0990
"	"	"	4 "	" "	.1012
"	"	"	over night	" "	.1036
"	"	"	" "	" "	.1036

Since in all of the above only one experiment ran as much as 1% too low, it would appear that barium oxalate can be quantitatively converted to sulphate in from two to twelve hours, depending upon the temperature and the number of occasional stir-

* Sidersky, Zeit. f. Anal. Chem. **22**, 10, (1883).

rings given the mixture. It is also noticeable that when treated with hydrochloric acid which is too strong or when the treatment is continued too long the results are high. Since this would seem to be due to the fact that some of the barium sulphate is dissolved by the hydrochloric acid, three more experiments were run in the same way and using the same amounts of barium and calcium carbonates, but in these, after the hydrochloric acid treatment the solution was nearly neutralized with ammonia, then brought to boiling and a drop of sulphuric acid added. The solution was well stirred, allowed to cool and filtered after setting aside about an hour. The dissolved barium sulphate was thus reprecipitated. .1004, .1002 and .1003 grams of CaO were found. It will be noted that the blanks gave .1001 and .1001, as shown in previous table. This procedure is therefore quite accurate, especially if the usual precautions for precipitating barium sulphate are observed when the drop of sulphuric acid is added. If, however, the solution is not heated, if allowed to remain too strongly acidified with hydrochloric acid, and if the solution is not well stirred and then allowed to set until the reprecipitated barium sulphate becomes granular enough to be retained on the filter, the results will be too high.

There is one decided advantage of this method. Barium sulphate formed by the conversion of barium oxalate to the sulphate is coarsely granular, settles at once and has no tendency whatever to run through the filter. It is one of the easiest of all precipitates to filter and wash.

METHOD FOR THE SEPARATION OF CALCIUM FROM BARIUM

The method which was used in the analyses of silicates and which is recommended for the quantitative estimation of calcium in the presence of barium, (especially if large amount of barium is present), is as follows:

Bring the solution to boiling, make ammoniacal and add ammonium oxalate until precipitation is complete. Calculate the amount of sulphuric acid necessary to convert all of the barium present to barium sulphate, dilute and neutralize with ammonia. To the solution containing the mixed oxalates add the ammonium sulphate solution and stir well. Allow this to stand for about two hours, stirring at intervals. The solution may be kept hot, but this is not necessary. Longer standing will do no harm. By the end of this time all of the barium oxalate will have been converted into barium sulphate, while the calcium oxalate will remain unchanged. Filter and wash the precipitate, observing the usual

precautions for washing calcium oxalate. The solution should be cold and the precipiate is best washed at first with a dilute solution of ammonium oxalate and then with water. Set filtrate aside for the determination of magnesium. After the precipitate has been thoroughly washed, the filter paper is unfolded against the back of the original beaker and by carefully directing the stream from the wash bottle, all of the precipitate can be washed back into the beaker. Add hydrochloric acid somewhat in excess of the amount necessary to dissolve the calcium oxalate. Set aside for at least one hour, stirring at intervals. The reaction may be hastened by heating, but this is unnecessary if sufficient time is allowed. When the action is complete dilute to about 250 cc. Add ammonia until the solution is almost, but not completely neutralized, bring the solution to boiling and add one drop of sulphuric acid. As stated before, this is to reprecipitate any barium sulphate which may have been dissolved by too great an excess of hydrochloric acid. Stir vigorously, let set an hour or two, filter and wash thoroughly with water. Discard the precipitate which consists only of barium sulphate and determine the calcium in the filtrate in the usual way.

In the analyses given below the calcium was precipitated as oxalate, and, after ignition, weighed as oxide. There is, however, no reason why the volumetric method could not be used.

That the method is accurate is shown by the following analyses. In the one column are given the results obtained by the usual method of decomposing the silicate by alkali carbonate, in the other the results by decomposing by barium salts and determining by this method.

	Per cent CaO	
Sample	Na_2CO_3 decomposition	Ba salt decomposition
No. 1	2.38	2.36
No. 2	4.67	4.67
No. 3	3.73	3.71
No. 4	2.76	2.69
No. 5	1.79	1.79
No. 6	3.55	3.44
No. 7	5.34	5.26

ALKALIS

Two lots of barium carbonate were made and purified. Blanks run on both of these showed them to contain less alkali than the calcium carbonate used, and also less than the amount which, according to Hillebrand*, is usually found in purified reagents for the J. Lawrence Smith method.

* Hillebrand Analysis of Silicate and Carbonate Rocks, Bull. No. 422, U. S. G. S., 171.

All of the rock samples were decomposed without difficulty by the J. Lawrence Smith method, except No. 1, a pink tourmaline, which left a considerable gritty residue. This could not be due to the size of the particles, for after passing through the finest bolting cloth, this sample was subjected to a long grinding in the agate mortar. No other sample was given this extra grinding. A larger portion of ammonium chloride and calcium carbonate was used, but without success. Only when heated to a bright redness with about 50% excess of the reagents could this specimen be decomposed by the J. Lawrence Smith method. A fusion then took place and since the temperature was above that which is necessary to volatilize both potassium and lithium chlorides, it is quite certain that some of these were lost. With the barium salts the decomposition was complete, no gritty particles could be found. The other samples decomposed completely by both methods. It is therefore evident that the barium salt method has two advantages over the J. Lawrence Smith method;; first, the barium salts produce a complete decomposition where the J. Lawrence Smith method in certain cases will not; second, the reagents can be prepared more free from alkalis.

The melting points of the alkali chlorides given by different investigators* vary according to the method employed in determining the melting point. Ramsey and Eumorfopoulous give that of lithium chloride as 491°, potassium chloride 762° and sodium chloride 792°. Abegg† states that at its melting point, lithium chloride has a measureable vapor pressure. If this statement be correct, there must be some loss in the usual method of determining lithium chloride and very likely some in determining potassium chloride, as the method calls for three heatings where there is a serious danger of loss, first, during the decomposition; second, when the crucible is heated just to a perceptible redness to drive off the ammonium chloride and ammonium carbonate, and finally, when the crucible is again heated to a perceptible redness to drive off the last traces of these just before weighing. Heating the silicate to a temperature that will decompose it undoubtedly goes beyond 491°, and again heating the nearly pure alkali salts to a point where the redness can be seen again goes above the temperature where lithium chloride has a noticeable vapor pressure.

*Landolt-Bornstein. Physikalisch-Chemische Tarbellen, 274-278.
†Abegg. Handbuch der Anorganischen Chemie **2**, 1, 122.

Experiments were made to avoid this loss. At first a method was tried by using two crucibles of different sizes. The decomposition mixture was placed in the smaller and the larger one was used as a cover. A circular hole was cut in a thick piece of asbestos board and the lower crucible allowed to project through the hole as far as the decomposition mixture extended, thus protecting the upper portion of the crucible from the direct heat of the flame. Through a flanged glass tube a current of air was blown into the upper crucible. Thus if any of the alkali chlorides were volatilized they would be condensed on the bottom of the upper crucible. A pad of calcium or barium carbonate, according to the method used was placed on top of the decomposition mixture and as great an air space as possible was left between this and the bottom of the upper crucible. While this method was to some extent efficient, in some cases it did not give satisfactory results.

The plan was then changed, using a current of water instead of air to cool the crucible used as a cover. To do this the two crucibles were used as before and a two-hole rubber stopper, cut off so as to leave as little rubber as possible exposed, was tightly fitted into the upper crucible. Two bent glass tubes passed through the holes, the one which reached near the bottom being covered by a short bit of rubber tube to protect the crucible from being scratched in case the glass tube is pressed against it. A slow current of water can then be passed through the upper crucible, which will cool it so thoroughly that any volailized salts will be condensed on its bottom. The lower crucible should go as far through the asbestos board as the contents of the crucible extend. The asbestos board must be thick enough to protect the rubber stopper. A pad of calcium or barium carbonate at least two millimeters in thickness must be placed on top of the decomposition mixture and an air space of at least five or six millimeters left between this and the bottom of the upper crucible, otherwise the heat will be radiated off so fast from the upper portion that this will be only partially decomposed. When set up in this way, the full heat of a large Meeker burner may be used and the crucible below the asbestos board heated to a bright redness without any loss of alkalis. When the J. Lawrence Smith method is used, on removing the outer crucible, a thick coating of ammonium chloride will be found on its bottom and a strong odor of ammonia given off from the ammonium carbonate formed.

Two precautions were found necessary in using this scheme. The pad of calcium or barium carbonate placed on top of the decomposition mixture must be of sufficient thickness to prevent too great a loss of heat and the cold water must not be run through

the crucible used as a condenser until it has become somewhat warm, otherwise atmospheric moisture will condense on the outside, run in on the mixture and by hydrolysis of the barium chloride at the high temperature, attack the crucible.

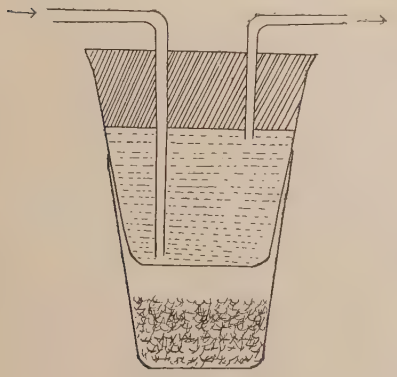

FIGURE I.

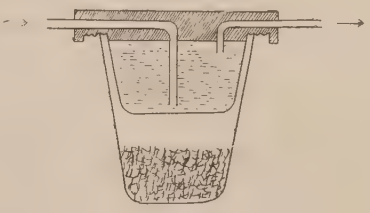

FIGURE II.

The simple arrangement described above is shown in Fig. I. The especially constructed lid as shown in Fig. II, is proposed where a large number of determinations are to be made. This can easily be made from copper and platinum or gold plated. The annoyance of singeing rubber stoppers would be avoided , while the corrugated edge projecting over the crucible would make it fit over any size crucible and at the same time serve as a greater condensing surface to any vapors of alkalis which might escape.

Since lithium chloride is lost when heated to 491°, instead of heating to perceptible redness after the first and second evaporations, the crucible was placed in an air bath and heated to 350-360° to drive off the ammonium salts. Since ammonium chloride dissociates at 250°, while ammonium carbonate volatilizes at a much lower temperature, it would seem unnecessary to heat higher. The procedure was found to be entirely satisfactory and to eliminate the risk of heating too high over an open flame, where all parts of the crucible are not equally heated and the degree of heat is at best only an approximation.

Experiments were made to determine whether any alkali salts were lost by the above procedure, using the water-cooled crucible and heating to a bright redness with a Meeker burner for one hour. 0.1 gram of specially purified potassium chloride, (used for conductivity research work in this laboratory), was mixed with 0.5 gram of a silicate found to be free from alkali. Follow-

ing this method 0.0995 and 0.0999 gram of potassium chloride was found, showing the small loss to be well within the limit of experimental error.

Owing to the difficulty of obtaining a pure unhydrolized lithium salt, a solution of lithium chloride was made up and kept in a glass-stoppered bottle. 10 cc. portions of this were taken for each experiment and evaporated to dryness in a platinum crucible. In the first series the amount of lithium was determined by Palkin's method, results being expressed as lithium sulphate. In the second series, to the lithium chloride solution, about two-tenths of a gram of each ammonium chloride and ammonium carbonate was added, the solution evaporated to dryness and the ammonium salts driven off by heating in the oven to 350° and the lithium determined in the same way. Results were as follows:

$LiCl+NH_4Cl+(NH_4)_2CO_3$	0.4465 and 0.4471 grams Li_2SO_4
LiCl alone	0.4475 and 0.4481 " "

There is a slight loss, but measuring so small an amount of so concentrated solution with a pipette may perhaps make this only an experimental error. The error in an actual rock analysis should be practically nothing, since here the excess of ammonium salts was far in excess of those ordinarily driven off and the amount of lithium salt is much greater than that found in any lithia silicates.

A comparison of the results obtained by the use of the two methods of decomposition is shown in the follow table:

	Li_2O		K_2O		Na_2O	
Sample	J. L. S.	Ba	J. L. S.	Ba	J. L. S.	Ba
No. 1		.0141		.0085		.0203
No. 2			.0017	.0017	.0107	.0107
No. 3			.0020	.0020	.0334	.0346
No. 4			.0044	.0044	.0308	.0308
No. 5			.0242	.0243	.0312	.0317
No. 6			.0000	.0000	.0037	.0047
No. 7			.0000	.0000	.0000	.0000

MAGNESIUM

Since the determination of magnesium is the same by both methods of decomposition of the silicate, the following table giving a comparison of the results of analyses by both methods will suffice.

	MgO	
Sample	Na_2CO_3	Ba salts
No. 1	.1078	.1079
No. 2	.2144	.2128
No. 3	.0039	.0037
No. 4	.0136	.0132
No. 5	.0183	.0164
No. 6	.0386	.0375
No. 7	.0228	.0238

OTHER ELEMENTS.

Other elements were determined on separate portions and consequently the results are only of interest in the summation of the analyses. Combined water was determined by the lead oxide method. Manganese was determined by the Volhard method—the permanganate solution being standardized against purified manganese sulphate. In all other cases the methods followed were those described by Hillebrand* and by Washington†.

SUMMATIONS

In the summations of anayses the constituents determined on separate portions are given in the column to the left. The first five samples were kindly furnished by Prof. Edward B. Mathews of the Geology Department. The last two samples, manganese silicates, were obtained from Dr. Joseph T. Singewald, also of the Geology Department.

NO. 1. TOURMALINE.

A partially transformed pink tourmaline from Texas, Md. The crystals were small and tightly imbedded in quartz and marble. The latter was chipped off as much as possible and then the remainder of the marble removed by hydrochloric acid. Most of the quartz was removed from the tourmaline before grinding. A few cystals of titanite were mixed with the tourmaline. The amount of the sample obtained in this way was small, and as much difficulty was experienced in decomposing it, the material was all used up before the analysis was completed. As stated before, the alkalis could not be determined by the J. Lawrence Smith method, because the decomposition in this way was incomplete.

	On separate samples	Na_2CO_3	Ba salts
SiO_2		39.06	39.16
Fe_2O_3		.96	.96
TiO_2		.78	.78
Al_2O_3		31.59	31.64
CaO		2.38	2.36
MgO		10.78	10.79
Li_2O			1.41
K_2O			.85
Na_2O			2.03
H_2O	.80		
B_2O_3	undet.		

* Hillebrand, Analysis of Silicate and Carbonate Rocks, Bull. No. 422, U. S. G. S.

† Washington, Chemical Analysis of Rocks, John Wiley & Sons, N. Y. (1914).

NO. 2. WEBSTERITE.

Websterite from one and a half miles southwest of Pleasant Grove, Md. One of the hardest specimens to decompose. Attacked crucible slightly.

	On separate samples	Na_2CO_3	Ba salts
SiO_2		52.18	52.18
Fe_2O_3		1.17	1.11
TiO_2		.64	.64
Al_2O_3		4.91	5.01
Al_2O_3		4.67	4 67
MgO		21.44	21.28
Na_2O		1.07 (J. L. S.)	1.07
K_2O		.17 (J. L. S.)	.17
FeO	11.62		
Cr_2O_3	.27		
P_2O_5	.22		
H_2O+	.19		
$H_2O—$	1.80		
MnO	none		
S	.04	14.14	14.14
Co	trace		
Zr O_2	none		
F.	trace		
Total		100.39	100.27

NO. 3. META-RHYOLITE

From Susquehanna Bridge, Maryland.

	On separate samples	Na_2CO_3	Ba salts
SiO_2		76.61	76.51
Fe_2O_3		1.04	1.04
TiO_2		.20	.20
Al_2O_3		12.73	12.83
CaO		3.73	3.71
MgO		.39	.37
Na_2O		3.34 (J. L. S.)	3.46
K_2O		.20 (J. L. S.)	.20
FeO	1.74		
$H_2O,110°+$	.00		
$H_2O,110°—$	.18		
MnO	.20		
Zr O_2	.00		
P_2O_5	.00		
Cr_2O_3	.00	2.12	2.12
Total		100.18	100.26

NO. 4. GNEISSIC INCLUSION.

Light gray gneissic inclusion in biotite granite from one-half mile northwest of Triadelphia, Md.

	On separate samples	Na_2CO_3	Ba salts
SiO_2		78.05	77.99
Fe_2O_3		.93	.93
TiO_2		.66	.66
Al_2O_3		10.27	10.39
CaO		2.76	2.69
MgO		1.36	1.32
Na_2O		3.08 (J. L. S.)	3.08
K_2O		.44 (J. L. S.)	.44
FeO	2.24		
S	.01		
$Zr\ O_2$	.09		
H_2O,110°+	.34		
H_2O,110°—	.12		
P_2O_5	.02		
Cr_2O_3	.00		
MnO	.00	2.82	2.82
Total		100.37	100.34

NO. 5. LIGHT BAND IN GNEISS.

Light fine-grained band in gneiss from Springfield Roller Mill, Piney Run, Md.

	On separate samples	Na_2CO_3	Ba salts
SiO_2		69.70	69.67
Fe_2O_3		1.08	1.08
TiO_2		1.12	1.12
Al_2O_3		11.48	11.64
CaO		1.79	1.79
MgO		1.83	1.64
Na_2O		3.12 (J. L. S.)	3.17
K_2O		2.42 (J. L. S.)	2.43
FeO	4.19		
H_2O,110°+	.60		
H_2O,110°—	.13		
S	.31		
$Zr\ O_2$	1.95		
P_2O_5	.19		
Cr_2O_3	.00	7.37	7.37
Total		99.91	99.91

NO. 6. QUELEUZITE.

A queleuzite from Brazil. After the iron and aluminum hydroxides were reprecipitated in this sample, the filtrate was put into volumetric flask and the manganese precipitated by ammonium sulphide. When precipitation was complete and the precipitate had settled, an aliquot part was removed by a siphon and the calcium and magnesium determined in this. The manganese was determined by the Volhard method, the permanganate used

being standardized against purified manganese sulphate. The manganese was also determined by the chlorate method, (Hempel), and a close check obtained.

	On separate samples	Na_2CO_3	Ba salts
SiO_2		9.38	9.39
Fe_2O_3		.00	.00
TiO_2		.29	.29
Al_2O_3		2.66	2.64
CaO		3.55	3.44
MgO		3.86	3.75
Na_2O		.37 (J. L. S.)	.42
K_2O		.00 (J. L. S.)	.00
FeO	3.42		
MnO	50.68		
H_2O,110°+	.60		
H_2O,110°—	.00		
CO_2	25.26		
$Zr O_3$	.38		
NiO	traces	80.34	80.34
Total		100.48	100.48

NO. 7. GARNET ROCK

A garnet rock from Brazil. The same method for determining manganese, calcium and mangnesium was used as in No. 6.

	On separate samples	Na_2CO_3	Ba salts
SiO_2		37.01	37.07
Fe_2O_3		.00	.00
TiO_2		1.09	1.09
Al_2O_3		19.44	19.32
CaO		5.34	5.26
MgO		2.28	2.38
Na_2O		trace	trace
K_2O		trace	trace
FeO	7.13		
MnO	27.20		
CO_2	.00		
H_2O,+110°+	.28	34.36	34.36
H_2O, 110—	.15		
Total		99.92	99.88

CONCLUSIONS

1. Silicate rocks can be completely decomposed by heating with a mixture of barium carbonate and chloride. For a one-gram sample of rock powder, five grams of the salts in the ratio of four moles of carbonate to 1 mole of anhydrous chloride heated over an ordinary Bunsen burner for one-half to one hour is sufficient.

2. The method has an advantage over the sodium carbonate decomposition, as the mass sinters together instead of melting. This prevents loss by spattering. The sintered cake is more easily removed from the crucible than the sodium carbonate fusion.

3. Silicates may be decomposed in this way, which cannot be decomposed by the J. Lawrence Smith method. The method can therefore be used for the determination of alkalis where the J. Lawrence Smith method cannot be used.

4. A method is described by which small quantities of calcium may be quantitatively determined in the presence of large quantities of barium.

5. Barium can be completely removed from a solution by precipitating as an oxalate and transforming the oxalate to sulphate. The barium sulphate thus formed can be filtered without the slightest difficulty.

6. A method is described by which a high heat may be used in the decomposition of silicates for the determination of alkalis, without loss of the alkalis.

7. Results of analyses are given which agree closely with the results obtained by the best methods now in use.

BIOGRAPHICAL

The author was born at Glen Morris, Md., October 17, 1876. His early education was received in the public school at Reisterstown, Md. In 1893 he entered the Maryland Agricultural College and was graduated with the B. S. degree in 1897. For sixteen years he was engaged in the work of teaching: From 1899-1905 in public high schools of Maryland, Virginia and Georgia; 1905-'07, instructor in science, Anne Arundel Academy, Millersville, Md.; 1907-'11, instructor in science, Bellefonte, (Pa.) Academy; 1911-'15, professor of chemistry, Albright College, Myerstown, Pa. During 1908-'10 he pursued special work in analytical chemistry in Penna. State College. The summer sessions of 1908, '09, '10, '11, '12, '13 and '14 he pursued graduate courses in chemistry at Columbia University, from which he received the A. M. degree in 1912. He entered the Johns Hopkins University in 1915, taking chemistry as major subject, physical chemistry and biological chemistry as subordinates. During 1915-'16 he was laboratory assistant in the undergraduate department; 1916-'17 he held a Hopkins scholarship.